

Microheterogeneities in Ionic Liquids – Kinetics and Recent Observation

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The question of mesoscopic heterogeneities in liquid phases is a long standing problem, which received renewed interest in recent years. Some of the observations were implicated with aggregation, micellar kinetics or as, in the case of tertiary butyl-alcohol recently reported [1], with the formation of clathrate-structures in solution. Heterogeneities on both a microscopic and a mesoscopic scale were predicted by simulations and observed by spectroscopic and scattering techniques in organic salts with melting points near or below room temperature [2] - termed "Ionic Liquids" (ILs), which became an important research topic during the last decade. Similar findings were reported, already in the late sixties in connection with investigations of critical phenomena in mixtures [e.g., 3]. Meanwhile -after some years of unclear trial and error science with big uncertainties - the discussion is becoming respectable. For ILs systematic studies of thermodynamic and thermophysical properties of ILs and their solutions provoked questions concerning the existence of mesophases, partially ambiphilic behavior or singularities in the parameter space. As a result coordinated research programs or joined research focusing on these problems were initiated within the IL-community. These scientific efforts have led to a number of theoretical and experimental results. In this context molecular dynamics simulations [e.g., 4] have predicted a microscopic separation of ILs into regions formed by the ionic parts and non-ionic parts of the ILs. Such non-uniformities, which are in the scale of few nanometers, have been corroborated by X-ray or neutron scattering [5, 6] and other spectroscopic methods. Much larger non-uniformities with typical sizes above 100 nanometer (up to a μm) were observed by light-scattering investigations of solutions of ILs in non-ionic solvents [7]. Such long-range structures resulting in a manifold kinetic behavior of the solutions, showing evidence of a decay of long-range structures after several hours or even days or weeks. Taking those fluctuations into account is important, e.g., when investigating crossover from Ising to mean-field critical behavior [8,9] or other effects related to a structuring in the liquid.

We report light-scattering experiments on the neat ionic liquid $\text{C}_{12}\text{mimNTf}_2$ (1-dodecyl-3-methylimidazolium(bistrifluoromethylsulfonyl)amide) that give evidence of non-uniformities on a mesoscopic scale that may be regarded as structures analogous to the Weiss areas of magnets or the domains in liquid crystals. The fluctuations are characterized by static and dynamic light scattering measurements over a period of typically 10 days as function of pressure and temperature. Additional kinetic studies applying fast pressure changes on the ILs are performed. After the decay of the initial non-equilibrium non-uniformities the remaining scattering is regarded as characteristic property of the fluid, which is described and interpreted. First results suggest an analogy by the behavior of the fluids with a glass-transition.

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